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(54) IMPROVEMENTS IN OR RELATING TO PROCESSES FOR THE MANUFACTURE OF ALUMINIUM ARTICLES COATED WITH METALS

(71) We, ASSOCIATED ELECTRICAL INDUSTRIES LIMITED, of 1 Stanhope Gate, London W1A 1EH, a British Company, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to processes for the manufacture of articles of aluminium, and aluminium-based alloys, having on their surfaces continuous adherent coatings of other metals, and is more particularly concerned with a method of cleaning and conditioning the said surfaces before the application of such coatings.

As is well known, difficulties arise in forming adherent metal coatings on aluminium, due to the tenacious oxide layer which is always present on aluminium surfaces. Since the presence of any oxide film will cause a metal coating to flake off, it is essential to remove the oxide layer completely before the application of the coating, and to deposit a metal layer immediately after removal of the oxide, before re-oxidation of the aluminium surface can take place. Suitable metal coating processes include, for example, immersion of the aluminium article in a bath of molten metal, of sufficiently low melting point, and electroplating. Some chemical processes for removing the oxide layer prior to such coating processes have been proposed, but these oxide removal processes are usually somewhat elaborate and too slow to be suitable for application to continuous coating processes such as, for example, the production of tin- or copper-coated aluminium wire.

It is an object of the present invention to provide an improved process for forming a continuous adherent metal coating on an aluminium (or aluminium-based alloy) article, and in particular to provide an improved method of cleaning and conditioning the aluminium surface, for removal of an oxide layer and maintaining an oxide-free surface, preparatory to the metal coating procedure, which cleaning and conditioning method can be carried out rapidly so as to be applicable, for example, to a continuous process for tinning aluminium wire.

According to the invention, a process for the production of an article of aluminium, or of an aluminium-based alloy, having a continuous adherent coating of metal on the surface thereof, consists of the steps of subjecting the said surface to an etching treatment by immersion in an aqueous solution of ammonium bifluoride ($NH_4F.HF$) of concentration from 10 to 100 grams of ammonium bifluoride per litre of solution, with or without a simultaneous or subsequent conditioning treatment consisting in immersion in a conditioning solution consisting of a nickel salt and a zinc salt in an acidic aqueous medium, said aqueous solution of ammonium bifluoride either containing no other constituents or, for carrying out a said conditioning treatment simultaneously with the etching treatment, containing only the said constituents of the conditioning solution in addition to ammonium bifluoride, rinsing said surface with water immediately after said treatment or treatments or each of said treatments, and applying a metal coating to said surface immediately after the last said rinsing step.

The concentration of the ammonium bifluoride solution employed for the etching treatment is preferably between 20 and 60 grams per litre, 37.5 grams per litre for example being suitable. The etching solution cleans and degreases the aluminium (or aluminium-based alloy) surface and removes the oxide layer completely, having a rapid action even at room temperature, but preferably the solution is heated, suitably to 60°C, to increase the speed of the action: at this temperature, immersion of the aluminium article in the solution for 10 seconds

is usually sufficient, but longer immersion times will be required at lower temperatures. If desired, a preliminary conventional cleaning of the aluminium surface to remove grease and dirt can be carried out, before the etching treatment.

In some cases a metal coating may be applied to the aluminium surface immediately after the etching treatment, without any further preparatory treatment of the surface, the etchant solution being rinsed off with water prior to the coating procedure. However, it is usually preferred to subject the aluminium surface to a conditioning treatment as aforesaid, in a solution of a nickel salt and a zinc salt in a suitable acidic liquid medium, either subsequently to or simultaneously with the etching treatment. For the conditioning treatment, an aqueous solution of ammonium bifluoride of a concentration similar to that of the etchant solution is conveniently used as the acidic medium for the nickel and zinc salts, to avoid cross-contamination of the etchant and conditioning solutions which might result if a different acidic substance were used in the latter, and to eliminate the need for an intermediate rinse between the etching and conditioning steps; in addition, a further etch cleaning of the surface is effected by the presence of ammonium bifluoride in the conditioning solution.

A preferred solution for use for a conditioning treatment immediately following the etching treatment, without an intermediate rinse, consists of nickel chloride at a concentration of 1 to 200 grams per litre, and zinc sulphate or zinc chloride at a concentration of 0.1 to 50 grams per litre, in an aqueous ammonium bifluoride solution as aforesaid. The aluminium or aluminium-based alloy article is immersed in this solution for 5 to 15 seconds, at room temperature, the length of time required depending upon the actual ambient temperature.

Alternatively, the etching and conditioning treatments can be combined in a single step, by adding to the ammonium bifluoride etchant solution salts of nickel and zinc in the concentrations specified above, together with concentrated hydrochloric acid in a concentration of 25 ml per litre of the solution. The aluminium or aluminium-based alloy article may be immersed in this combined etching and conditioning solution for 5 to 15 seconds, again depending upon the ambient temperature. It should be noted that a simultaneous etching and conditioning treatment can be carried out satisfactorily only if the aluminium article is of good surface quality, that is to say free from grease, dirt, solvents and detritus.

The etching treatment of the invention, either alone or followed by or combined with a conditioning treatment as described above, is particularly suitable for preparing aluminium or aluminium-based alloy surfaces to be coated with tin, either by immersion in molten tin or by electroplating. However, aluminium or aluminium-based alloy articles processed by the method of the invention can be plated with any desired metal.

The aluminium or aluminium-based alloy articles can be coated with tin immediately after the ammonium bifluoride etching treatment and a water rinse, without a conditioning treatment, by immersion in a bath of molten tin subjected to ultrasonic agitation. If desired, however, a conditioning treatment as specified above can be carried out prior to such immersion.

If an aluminium (or aluminium-based alloy) article is to be electroplated, the said conditioning treatment is preferably employed in addition to the etch cleaning treatment. Preferably also, if the article is to be plated with tin, the treated aluminium surface is first plated with copper, in order to give improved adhesion of the tin coating. Known plating baths may be employed for the deposition of both the copper and the tin: suitable plating baths are, for example, an alkaline copper pyrophosphate or an alkaline copper cyanide solution, and a bright acid tin plating solution for the deposition of tin either directly on the aluminium or aluminium-based alloy surface or on a preliminary coat of copper.

In another alternative process for coating an aluminium or aluminium-based article with tin, the surface of the article is subjected to both the etching treatment and the conditioning treatment in accordance with the invention, is then plated with a thin layer of copper, and is finally coated with tin by immersion in the molten metal, without ultrasonic agitation.

The processing method of the invention is particularly advantageous for use in a continuous process for tin-coating aluminium wire, since the removal of the surface layer of oxide is effected rapidly thereby, so that wire can be passed continuously, at a conveniently rapid rate, through an ammonium bifluoride etching bath, followed by or combined with a conditioning bath as aforesaid if required, a copper plating bath if required, and a tin plating bath or a molten tin bath, in succession, with water rinses at appropriate stages in the process, that is to say following the etching bath or the conditioning bath if used, and after each metal coating bath.

One preferred process, in accordance with the invention, for coating aluminium, or aluminium-based alloy, articles with tin, will now be described in the following specific example.

In the process of the example, the article is first cleaned and etched by immersion in an aqueous solution of ammonium bifluoride of concentration 37.5 grams per litre, maintained at a temperature of 60°C, for 10 seconds, and is then immediately transferred to an aqueous conditioning solution containing 37.5 grams of ammonium bifluoride, 160 grams of nickel chloride dihydrate and 6 grams of zinc sulphate, per litre, is retained in this solution at room temperature for 5 to 10 seconds, and then rinsed with water at room temperature for 2 to 5 seconds.

The treated aluminium article is then electroplated with copper by one of two methods, employing either a pyrophosphate or a cyanaide solution. In the first method, the plating solution consists of 94 to 119 grams of copper pyrophosphate, 300 to 375 grams of potassium pyrophosphate, 1 to 3 ml of 0.880 ammonia, and water to make up the solution to a litre, the ratio of P_2O_7: Cu in the solution being from 6.41 to 7:1 and the pH of the solution being from 8.6 to 8.9. The solution is maintained at a temperature of 55° to 60°C, and electric current of a magnitude to give a current density of not less than 20 mA/cm² at the surface to be plated is passed for a sufficient length of time to deposit a copper coating of the required thickness, for example one minute at a current density of 20 mA/cm² to give a coating 0.6 micrometre thick.

The plating solution employed for the second copper plating method consists of 55 grams of copper cyanide, 67 grams of sodium cyanide, 40 grams of Rochelle salt, 30 grams of sodium carbonate, and water to a litre. The solution is maintained at a temperature of 60° to 70°C, and deposition of copper is effected by passage of an electric current at a current density not greater than 30 mA/cm² at the plated surface, for example for one minute at 30 mA/cm² to give a copper coating 0.8 micrometre thick.

On completion of the copper plating step, the article is rinsed with water for 5 seconds at room temperature, and is then immersed in a proprietary aqueous bright acid tin plating bath, for example a solution manufactured by Imasa Silvercrown Limited, containing 28 to 31 grams of tin, 112 to 138 grams of free sulphuric acid and 40 ml of an unspecified addition agent, per litre. The solution is maintained at room temperature during the passage of an electronic current at a current density of not less than 20 mA/cm² at the surface being plated. The process is continued, for example, for one minute at a current density of 20 mA/cm² to give a tin coating of thickness 0.5 micrometre. The plated article is finally rinsed in water for 5 seconds at room temperature.

The process of the example can be applied to the continuous tinning of aluminium wire, by passing the wire, at a conveniently rapid rate, successively through vessels containing respectively the etchant solution, the conditioning solution, a copper plating solution, and the tin plating solution, each maintained at the required temperature, and with the provision of rinsing water after the respective steps of conditioning treatment, copper plating, and tin plating.

WHAT WE CLAIM IS:—

1. A process for the production of an article of aluminium, or of an aluminium-based alloy, having a continuous adherent coating of metal on the surface thereof, which consists of the steps of subjecting the said surface to an etching treatment by immersion in an aqueous solution of ammonium bifluoride ($NH_4F.HF$) of concentration from 10 to 100 grams of ammonium bifluoride per litre of solution, with or without a simultaneous or subsequent conditioning treatment consisting in immersion in a conditioning solution consisting of a nickel salt and a zinc salt in an acidic aqueous medium, said aqueous solution of ammonium bifluoride either containing no other constituents or, for carrying out a said conditioning treatment simultaneously with the etching treatment, containing only the said constituents of the conditioning solution in addition to ammonium bifluoride, rinsing said surface with water immediately after said treatment or treatments or each of said treatments, and applying a metal coating to said surface immediately after the last said rinsing step.

2. The process according to Claim 1, wherein the concentration of the ammonium bifluoride solution employed for the etching treatment is between 20 and 60 grams per litre.

3. The process according to Claim 1 or 2, wherein for carrying out the said etching treatment the ammonium bifluoride solution is heated to a temperature of 60°C.

4. The process according to any preceding Claim, wherein a preliminary cleaning of said surface to remove grease and dirt is carried out before the said etching treatment.

5. The process according to any preceding Claim, wherein a said conditioning treatment is carried out subsequently to the etching treatment, and wherein the said acidic medium is an aqueous solution of ammonium bifluoride of a concentration similar to that of the solution used for the said etching treatment, the conditioning solution contains nickel chloride at a concentration of 1 to 200 grams per litre of solution, and zinc sulphate or zinc chloride at a concentration of 0.1 to 50 grams per

litre of solution, and the aluminium or aluminium-based alloy article is immersed in said solution for 5 to 15 seconds at room temperature immediately following the said etching treatment, without an intermediate rinse.

6. The process according to any of the preceding Claims 1 to 4, wherein a said conditioning treatment is carried out simultaneously with the etching treatment, by employing for the etching treatment a said aqueous solution of ammonium bifluoride containing nickel and zinc salts in the concentrations specified in Claim 5, together with concentrated hydrochloric acid in a concentration of 25 millilitres per litre of solution, the aluminium or aluminium-based alloy article being immersed in said solution for 5 to 15 seconds at room temperature.

7. The process according to any preceding Claim, wherein the said metal coating formed on the treated aluminium or aluminium-based alloy surface consists of tin.

8. The process according to any of the preceding Claims 1 to 6, wherein the treated surface is coated with tin by immersion in a bath of molten tin subjected to ultrasonic agitation.

9. The process according to Claim 5 or 6, wherein a said metal coating is formed on the treated surface by electroplating

10. The process according to Claim 9, wherein the treated surface is first plated with copper and then with tin.

11. The process according to Claim 5 or 6, wherein the treated surface is first electroplated with copper and then coated with tin by immersion in molten tin.

12. A process according to any preceding Claim wherein, for the manufacture of tin-coated aluminium wire, aluminium wire is passed continuously and successively through an etching bath consisting of a said ammonium bifluoride solution, if required followed by or combined with a conditioning bath as specified in Claim 5 or 6, a copper plating bath if required, and a tin plating bath or molten tin, with water rinsing after passage through the etching bath, or through the conditioning bath if used, and after passage through each metal coating bath.

13. A process according to Claim 1, for the production of an article of aluminium or an aluminium-based alloy having a continuous adherent coating of tin on the surface thereon, carried out substantially as described in the foregoing specific example.

14. The process according to Claim 13 wherein, for the continuous production of tin-coated aluminium wire, the wire is passed successively through vessels respectively containing the etchant solution of ammonium bifluoride, the conditioning solution of ammonium bifluoride, nickel chloride and zinc sulphate, a copper plating bath, and a tin plating bath, with water rinsing after the respective steps of conditioning treatment, copper plating, and tin plating.

15. An article of aluminium or an aluminium-based alloy the surface of which has a continuous adherent coating of metal, manufactured by a process according to any of Claims 1 to 11 and 13.

16. Aluminium wire the surface of which has a continuous adherent coating of tin, or of copper and tin, manufactured by a process according to Claim 12 or 14.

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